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Fuchs et al.

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[54] **METHOD FOR OXIDATION-HARDENING METAL ALLOY COMPOSITIONS, AND COMPOSITIONS AND STRUCTURES THEREFROM**

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Related U.S. Application Data

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[52] **U.S. Cl.** ..... **148/11.5 R**; 75/153; 148/11.5 F; 148/32

[51] **Int. Cl.** **C22f 1/08**

[58] **Field of Search** ..... 75/153, 206, .5 BC; 148/11.5 F, 11.5 R

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[57] **ABSTRACT**

Relatively nonoxidizable metals and alloys, such as Cu, Ag and Au and their alloys, may be internally oxidation-hardened by forming therein discrete particles of a second phase containing a relatively oxidizable metal such as Zr, and heating the resultant alloy in an atmosphere sufficiently oxidizing to result in the formation of oxide particles therein.

3 Claims, 3 Drawing Figures

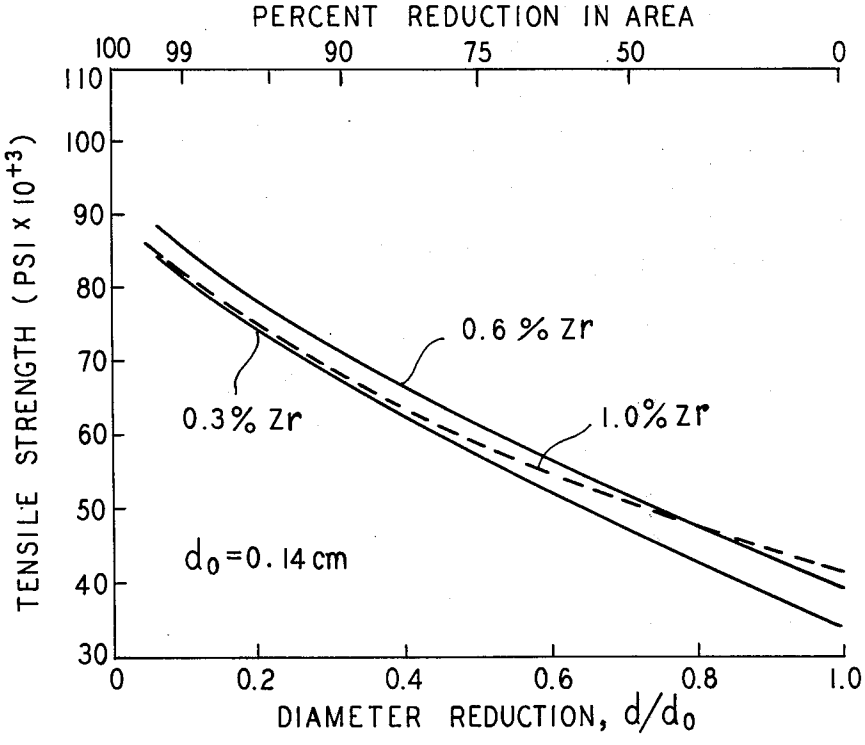


FIG. 1

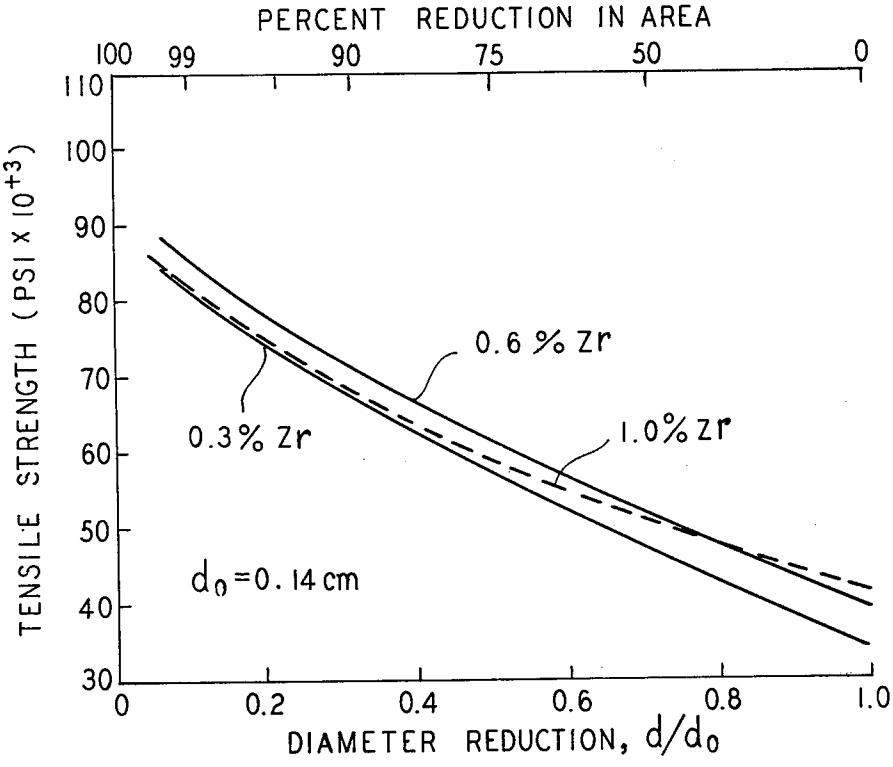


FIG. 2

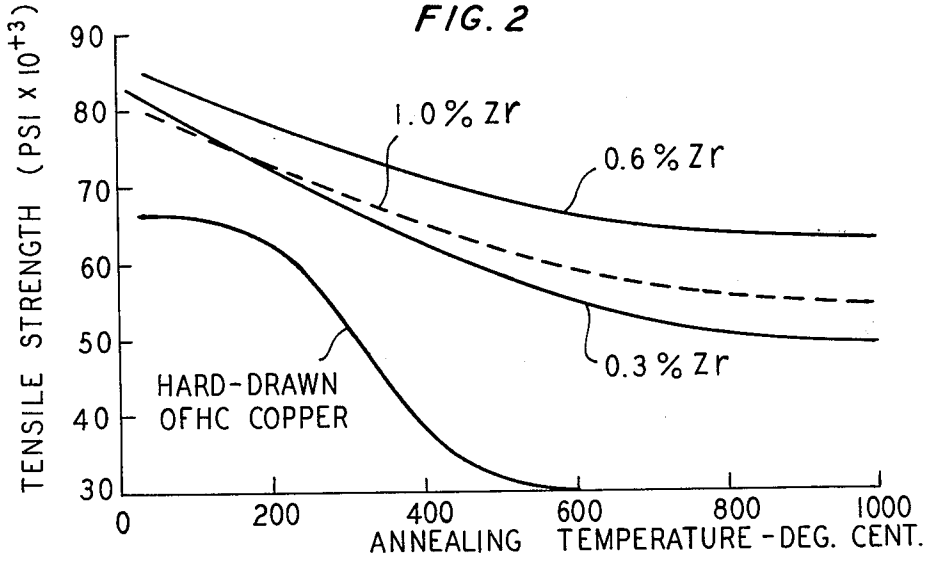
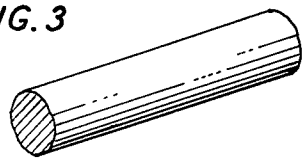


FIG. 3



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METHOD FOR OXIDATION-HARDENING METAL ALLOY COMPOSITIONS, AND COMPOSITIONS AND STRUCTURES THEREFROM

This application is a continuation of application Ser. No. 24,678, filed Apr. 1, 1970.

FIELD OF THE INVENTION

This invention relates to internally oxidation-hardened two-phase alloys, to a method for producing such alloys and to structures made therefrom.

PRIOR ART

It is known that increased strength and hardness may be imparted to solid solution alloys comprising solvent metals having relatively low heats of oxide formation and solute metals having relatively high heats of oxide formation, by heating the alloys in a medium that is oxidizing to the solute metals, but is relatively nonoxidizing to the solvent metals. Hardening is thus obtained by internal oxidation of the solute metal, i.e., by the precipitation of small oxide particles of the solute metal in the matrix of the solvent metal. Such hardening is a type of dispersion hardening known as internal oxidation-hardening.

Among the alloys which have been oxidation-hardened by the above technique are copper and silver alloys. A major disadvantage of this technique is that the solute metal tends to diffuse out towards the surface of the alloy to meet the inward-diffusing oxygen. Such tendency often leads to a layered structure and consequent embrittlement of the alloy. In extreme cases this tendency results in oxidation at the surface of the alloy with consequent failure of the hardening mechanism. In one instance, expensive powder metallurgy techniques were relied upon to minimize diffusion in a copper-beryllium oxide internally oxidation-hardened alloy. Such an approach is described in U.S. Pat. No. 3,184,835, issued to Charles D. Coxe et al. on May 25, 1965.

A second disadvantage in attempting to improve the mechanical properties of such alloys by oxidation-hardening lies in the fact that forming the required solid solution alloys lowers appreciably the electrical conductivities of the solvent metals. Any solute metal which is not oxidized during the subsequent heat treatment remains in the solvent metal, appreciably impairing the conductivity of the final body.

The search continues for economical and convenient ways to improve the mechanical properties of such metals and alloys, while maintaining the highest possible electrical conductivities.

SUMMARY OF THE INVENTION

It has now been discovered that internally oxidation-hardenable metals, such as copper, silver and gold and their alloys, may be oxidation-hardened by forming in the metal or alloy, discrete particles of a second phase containing a relatively oxidizable metal, such as zirconium, and heating the resultant alloy in an atmosphere sufficiently oxidizing to result in the formation of oxide particles therein. Oxidation-hardened Cu, Ag and Au and their alloys exhibit higher electrical conductivities than previously obtainable for oxidation-hardened single phase alloys of these metals, and are useful in a variety of applications, such as electrically conducting springs and cable, switch contacts, and welding tips.

Where the second phase is known to form a continuous network in a matrix of the first phase, discrete particles of the second phase may be obtained by quenching the molten alloy or mechanically working the alloy after it has solidified. In a preferred embodiment, quenching or working, or a combination of these, may be employed to reduce the size of discrete particles before oxidation and thus optimize the oxidation-hardening effect.

Other embodiments include the further enhancement of mechanical properties by combining other hardening mechanisms with oxidation-hardening. Accordingly, alloying ingredients and processing treatments after oxidation may be utilized to effect solid solution-hardening, precipitation-hardening and work-hardening.

One or more partial or full anneals may be employed at any stage of the processing, consistent with good metallurgical practice.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a graph of tensile strength (psi $\times 10^{+3}$) versus cold reduction after oxidation-hardening, expressed both as percent area reduction and diameter reduction, for three different alloy compositions of the invention;

FIG. 2 is a graph of tensile strength (psi $\times 10^{+3}$) versus annealing temperature (°C.) for three different oxidation-hardened alloys of the invention after an area reduction of 99 percent, and for hard-drawn copper; and

FIG. 3 is a perspective view of one embodiment of a structure of an alloy of the invention.

DETAILED DESCRIPTION

Metals and alloys which benefit from the inventive internal oxidation-hardening process include any metal which is relatively nonoxidizable and which is relatively permeable to oxygen. Such metals include those which are noted for use in applications requiring good to excellent electrical conductivities, such as copper, silver, gold and their respective alloys, containing most of the usual alloying elements, added for various reasons known to those skilled in the metallurgical arts. Harmful alloying elements include those which exhibit more than a limited solubility in the metals or alloys to be hardened, and which are relatively oxidizable, such as Be and Al in the case of copper. These elements should so far as possible be avoided and should in any event not exceed about 0.05 weight percent total.

Where it is desired to obtain optimum electrical conductivities for the alloys of interest, the total amount of alloying elements, exclusive of the oxidation-hardening elements, should be kept below about one weight percent total.

Although the presence of minor amounts of unintentional impurities in the alloys is not critical to the oxidation-hardening mechanism, for optimum conductivities, elements such as Fe, As and P should so far as possible be avoided, but should in any event generally not exceed about 0.02 weight percent total.

It is essential to the successful practice of the invention that the alloying element to be internally oxidized not only be relatively oxidizable, that is, form stable oxides but also exhibit limited solubility in the metal or alloy to be hardened, and thus participate in the formation of a second phase in the metal or alloy. For Cu, Ag and Au and their alloys, such elements include Zr, Hf, the Group IVB lanthanide series rare earths, including

Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and the Group IVB actinides, including Th, Pa and U. Of these, Zr is preferred for its availability and economy.

These elements in general tend to form intermetallic compounds with the Cu, Au or Ag. Although not a necessary part of this description, some of the compounds formed with copper are as follows: $ZrCu_3$, Hf_2Cu, $CeCu_6$, $PrCu_6$, UCu_5, $DyCu_4$, $GdCu_5$, $PuCu_{11}$, $SmCu_5$. These elements should not be present in the alloy in amounts greater than about 1 weight percent total, beyond which a nonuniform structure may develop, which could appreciably impair conductivity. In addition, above one weight percent, the formation of some large oxide particles is favored, which could impair mechanical properties. In general, amounts of from 0.1 to 0.6 weight percent are preferred, below which significant oxidation-hardening is not obtained, and above which structural uniformity and small particle size are no longer favored.

Where the strength or hardness requirements of a particular application are not obtainable by internal oxidation-hardening alone, further increases in strength and hardness may be obtained by the employment of one or more supplementary hardening mechanisms, such as solid solution-hardening or precipitation-hardening, or work-hardening. Up to 1 weight percent total of one or more precipitation-hardening or solid solution-hardening elements, such as Cd, Zn or Sn, may be added, the exact amount being determined not only by strength and hardness requirements, but also by conductivity requirements, since some decrease in conductivity is expected upon addition of one or more of these elements. The low temperature heat treatment required to effect precipitation-hardening may be carried out after oxidation-hardening and preferably prior to any work-hardening, to effect the desired enhancement of mechanical properties. Precipitation-hardening conditions are well known, and thus not necessary to this description. However, typical treatments could be from 150° to 350° C. for 2 to 20 hours.

Once internal oxidation-hardening (and any supplementary solid solution or precipitation-hardening) has been effected, further enhancement of properties may be had by working.

Although well known to those skilled in the art, it is noted that carefully controlled anneals, carried out subsequent to any of the hardening steps, while reducing to some extent the increased strength and hardness, nevertheless result in at least partial recovery of any ductility or conductivity lost during hardening. To aid the practitioner, data obtained for supplementary hardening and annealing conditions typical of the alloys of the invention are included in the examples.

Formation of the required two-phase alloys may result for some alloys in the second phase being distributed throughout the alloy body in the form of a continuous network. This second phase must be obtained as or converted to discrete particles, preferably of small size and close interparticle spacing. For the Cu-Zr alloy system, it has been found that particles about one micron or smaller in size and having an interparticle spacing of about 0.5 micron or smaller are preferred for effective oxidation-hardening to occur. The production of such discrete particles may be accomplished by quenching the molten alloy or by mechanically working the alloy after solidification. Quenching may be by chill casting, atomization, or other suitable method, provided it results in a cooling rate of at least 1000° C. per minute. Mechanical working (by any of the known methods such as rolling, swaging, drawing) must be by an amount equivalent to an area reduction of at least 90 percent, or a diameter reduction of about 0.3. Diameter reduction is defined as d/d_0, where d is the final diameter and d_0 is the initial diameter. Area reduction for sheet and strip is defined as

$$A = \frac{t_0 - t}{t_0} \times 100 , \qquad (1)$$

where t_0 is the initial thickness and t is the final thickness. It is preferred for the achievement of optimum properties to obtain as finely divided and uniform a dispersion of the second phase as possible, consistent with good metallurgical practice.

Oxide particles may be obtained from the discrete particles by heating the alloy in an oxygen-containing atmosphere. For copper-based alloys, this may be carried out at a temperature of from about 700° to about 960° C. at an oxygen partial pressure of about 10^{-5} to 10^{-10} atmospheres, the higher oxygen pressures corresponding to the higher temperatures. Above 960° C., the likelihood exists that partial melting of the alloy may occur, while below 700° C., the rate of internal oxidation is impractically slow. Above an oxygen partial pressure of 10^{-5} atmospheres in the heating atmosphere, surface oxidation of the alloy to be hardened is likely, while below 10^{-10} atmospheres, the rate of internal oxidation is impractically slow.

The rate of internal oxidation of cylinders or wires of the alloys of the invention may be described by the following equation:

$$\frac{(r_1)^2}{2} - (M_2)^2 \left[\ln \left(\frac{r_1}{r_2} \right) + \frac{1}{2} \right] = D \frac{\%O}{\%Zr} \cdot \frac{91.2}{16} t , \qquad (2)$$

where r_1 is the radius of the wire in centimeters, r_2 is the radius of the unoxidized core in centimeters, D is the diffusion coefficient of oxygen in copper in centimeters squared per second for the particular temperature, %O is the concentration of dissolved oxygen at the surface of the specimen in weight percent, %Zr is the initial zirconium content of the alloy in weight percent and t is the reaction time in seconds. By setting r_2 equal to zero in the above equation, the time for complete penetration, t_c is:

$$t_c = \frac{8}{91.2} \cdot \frac{\%\,Zr}{\%O} \cdot \frac{r_1^2}{D} . \qquad (3)$$

Although there is no limit to the size of a body which may be internally oxidation-hardened, practical considerations may dictate a maximum thickness, beyond which the time required for substantial oxidation is considered to be excessive. It should be noted that this time may be decreased by increasing either the heat

treatment temperature, or oxygen partial pressure, or both, within the limits already stated. These increases result in an increase in the diffusion coefficient, D, and the oxygen concentration, %O, in equations (2) and (3). For example, at 900° C. and an oxygen partial pressure of about 10^{-6} atmospheres, a copper rod about one-fourth inch in diameter containing 0.6 weight percent Zr may be substantially completely oxidation-hardened in about 80 hours, while at 960° C. and at the same oxygen partial pressure, the time is reduced to about 24 hours. It may be preferred to obtain optimum mechanical properties for the alloy of interest, and to this end a low temperature of treatment is preferred, since such promotes the formation of small oxide particles. Thus, a temperature should ordinarily be chosen to give the best mechanical properties consistent with a commercially acceptable treatment time.

Various methods for obtaining a controlled amount of oxygen in the heat treating atmosphere are known, and are therefore not a necessary part of this description. It is pointed out, however, that certain gas mixtures may for convenience be preferred, such as a helium-carbon dioxide mixture, which yields suitable oxygen partial pressures at relatively easily controlled ratios of the initial constituents. Where oxygen partial pressures near the lower limit specified above are desired, for example, to minimize the chance of oxidation of other alloying elements, it may be preferred to use a carbon monoxide-carbon dioxide mixture.

EXAMPLE 1

Alloys for internal oxidation were prepared by melting mixtures of high purity zirconium with copper in an induction furnace under a helium atmosphere. Melts containing 0.3, 0.6 and 1.0 weight percent zirconium were made, these melts all having zirconium contents greater than the maximum solubility of zirconium in copper. The insoluble portions were present as the intermetallic compound $ZrCu_3$. These melts were cast into bars 0.95 centimeters in diameter by 15 centimeters in length. The cast bars were then swaged and drawn to 0.14 centimeter diameter wire, corresponding to an area reduction of about 99 percent. These wires were internally oxidized in a controlled-atmosphere tube furnace at 900° C. The furnace contained a gas mixture of two parts helium and one part carbon dioxide, corresponding to an oxygen partial pressure of about 10^{-6} atmospheres. A series of photomicrographs of polished cross sections of the alloys were taken during the various stages of preparation. Photomicrographs of the as-case structure revealed a $ZrCu_3$ network surrounded by a copper alloy matrix. Photomicrographs of the wires formed by cold working showed that the $ZrCu_3$ network had been broken up into discrete particles of the order of about one micron in diameter. Electron micrographs of the wires after internal oxidation showed a dispersion of spherically shaped ZrO_2 particles in the size range from about 0.02 to 0.1 microns in diameter.

The mechanical and electrical properties of the internally oxidation-hardened alloys were examined before and after various degrees of cold working and after cold working to 99 percent reduction in area followed by annealing for 1 hour in hydrogen at various temperatures. Tensile strengths were obtained using a standard testing technique. FIG. 1 shows the variation of tensile strength with degree of cold working of internally oxidized wires. Tensile strengths before working, those obtained by internal oxidation-hardening alone, were about 35×10^3 to 42×10^3 psi, and compare favorably with those obtainable for copper, about 32×10^3 to 35×10^3 psi. It is seen that tensile strength values increase with degree of cold working, up to about 82×10^3 to 86×10^3 psi for 99 percent area reduction. Typical tensile strength values for hard-drawn copper are only about 50×10^3 to 65×10^3 psi. The curves for the 0.6 weight percent zirconium (1.30 volume percent ZrO_2) alloy and the 0.3 weight percent Zr (0.65 volume percent ZrO_2) alloy are nearly parallel, with the 0.6 weight percent alloy being about 4,000 psi stronger throughout. The 1.0 weight percent zirconium (2.16 volume percent ZrO_2) alloy was slightly stronger than the others before cold working but showed comparable strengths at high reductions.

The tensile strengths of hard-drawn copper and the same three alloys after drawing to 99 percent area reduction and annealing for one hour in hydrogen at various temperatures are compared in FIG. 2. It is seen that while the hard-drawn copper began to soften at 150° C. and was completely soft after annealing for 1 hour at 600° C., the oxidation-hardened alloys retained substantial tensile strengths up to 1000° C. Such data show that the alloys of the invention may find use in certain elevated temperature applications.

Percent elongation data were obtained on the 0.3 and 0.6 weight percent zirconium internally oxidation-hardened alloys, after a 99 percent area reduction and after a 99 percent area reduction followed by 1 hour anneals in hydrogen at 600° and 1000° C., respectively. The results are shown in Table I.

Table I

Alloy Composition (wt. % Zr)	Treatment After Oxidation Hardening	Percent Elongation (10.2 cm)
0.3	99% area reduction in each case	1.0
0.6		1.0
0.3	99% area reduction, 1 hr. anneal at	15.0
0.6	600° C. in each case	4.0
0.3	99% area reduction, 1 hr. anneal at	17.0
0.6	1000° C. in each case	10.0

It is seen that substantial recovery of ductility lost during cold working without substantial loss of tensile strength is obtainable for the alloys of the invention by annealing.

These mechanical properties are similar to those obtained for internally oxidation-hardened alloys produced by prior art techniques, such as the copper-beryllium oxide alloy mentioned above.

Electrical conductivity measurements were made using standard testing techniques on the 0.3 and 0.6 weight percent zirconium internally oxidation-hardened alloys after a 99 percent area reduction and after a 99 percent area reduction followed by annealing for one hour at 600° and 1000° C., respectively. Results are given in Table II in conductivity as a percentage of the International Annealed Copper Standard (IACS).

Table II

Alloy Composition (wt. % Zr)	Treatment after Oxidation-Hardening	Conductivity (% IACS)
0.3	99% area reduction in each case	97.4

Table II-continued

Alloy Composition (wt. % Zr)	Treatment after Oxidation-Hardening	Conductivity (% IACS)
0.6		90.6
0.3	99% area reduction, 1 hr. anneal in H_2	98.9
0.6	at 600° C. in each case	96.7
0.3	99% area reduction, 1 hr. anneal in H_2	92.9
0.6	at 1000° C. in each case	87.8
0.3	99% area reduction, 1 hr. anneal in	97.4
0.6	CO + 10% CO_2 at 1000° C. in each case	96.4

These conductivities are significantly higher than those obtainable for copper alloys internally oxidation-hardened by prior art techniques. For example, the copper beryllium oxide alloy mentioned above, when treated for 1 hour at 700° C., exhibited a conductivity of only about 85 percent IACS.

EXAMPLE 2

An alloy having the composition in weight percent, 0.6 percent zirconium, 0.5 percent cadmium, remainder copper was prepared as in Example 1, cast into a 1 inch diameter bar, and cold worked to a 0.25 inch diameter rod (94% area reduction). It was then internally oxidation-hardened by heating in an atmosphere containing carbon monoxide and carbon dioxide in the ratio of 1:10, at 980° C. for about 100 hours. The oxidation-hardened alloy was then work-hardened to 0.005 inch diameter (over 99% area reduction). While the conductivity of the final body was about 82% (IACS) versus 91% (IACS) for an identically treated alloy without the cadmium addition, substantial improvement in yield strength was realized by the cadmium addition, as shown in Table III.

Table III

	No Cd	0.5 Wt. % Cd
Tensile Strength (psi)	86,000	88,000
0.01% Yield Strength (psi)	47,000	60,000

Referring now to FIG. 3, there is shown an electrically conductive body 10 of an alloy of the invention.

The invention has been described in terms of a limited number of embodiments. However, since it essentially teaches the hardening of a two-phase alloy by internal oxidation, other embodiments are contemplated. For example, it may be preferred in some applications to strengthen or harden the surface portion only of an alloy of the invention, so that heating in an oxidizing atmosphere for a shorter time than required for complete oxidation-hardening to occur would be satisfactory. Furthermore, since the only requirements of the metals or alloys to be hardened are that they be relatively permeable to oxygen, yet relatively nonoxidizable, the invention is not limited to those metals and alloys which are noted for their electrical conductivities. For example, nickel and its alloys, which are widely used as magnetic materials, may be treated in accordance with the invention, in order to increase magnetic hardness or coercivity. It should be noted in this regard that effective increases in coercivity may generally be had from oxide particles of the order of three times the size of those required for effective mechanical-hardening.

As is known in the art, hardening may also be obtained by the formation of carbides and nitrides, as well as oxides, in the matrix alloy. In such cases, the advantages inherent in the use of a two-phase alloy system are substantially retained.

What is claimed is:

1. The method for producing an electrically conductive wire which method comprises:

solidifying a molten alloy of copper and from about 0.1 weight percent to about 1.0 weight percent of zirconium into a body in which said copper forms a first solid phase and said zirconium is present in an amount which forms a second solid phase of $ZrCu_3$,

mechanically working said body to a reduction in cross-sectional area whereby said second phase is dispersed as discrete particles within said first phase,

maintaining said mechanically worked body at a temperature of at least 700°C but below the melting point of the alloy in an atmosphere containing oxygen at a partial pressure between 10^{-5} and 10^{-10} atmospheres until oxidation hardening of the body has occurred over essentially the entire cross-section of said body, and drawing said body into wire of a reduced cross-sectional area.

2. The method of claim **1** wherein the said mechanical working of the body is equivalent to an area reduction of at least 90 percent.

3. The method of claim **1** wherein the body subjected to oxidation hardening is a rod having a diameter of the order of one-fourth inch.

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